

1. The Stark effect I have explained in class is the *quadratic* Stark effect: it obtains in the second order of the perturbation theory, so the energy shift  $\delta E$  is quadratic in the electric field  $\mathcal{E}$ ,  $\delta E \propto \mathcal{E}^2$ . However, some quantum systems exhibit a linear Stark effect where  $\delta E \propto |\mathcal{E}|$ , which obtains in the first-order of the degenerate perturbation theory when the unperturbed Hamiltonian  $\hat{H}_0$  has degenerate eigenstates with a non-zero matrix element of the electric dipole operator between them:

$$\hat{H}_0 |1\rangle = E_0 |1\rangle, \quad \hat{H}_0 |2\rangle = E_0 |2\rangle \text{ for the same } E_0, \quad \langle 1 | \hat{\mathbf{d}} | 2 \rangle \neq 0. \quad (1)$$

A good example of this behavior is the Hydrogen atom (or a hydrogen-like ion) without relativistic corrections: it has degenerate 2s and 2p quantum states (where 2 denotes  $n = 2$  while s denotes  $\ell = 0$  and p denotes  $\ell = 1$ ) with  $\langle 2s | \hat{\mathbf{d}} | 2p \rangle \neq 0$ . Similarly, the 3s, 3p, and 3d states are all degenerate while  $\langle 3s | \hat{\mathbf{d}} | 3p \rangle \neq 0$  and  $\langle 3p | \hat{\mathbf{d}} | 3d \rangle \neq 0$ , and likewise for  $n = 4, 5, \dots$

Let's focus on the  $n = 2$  energy level. For simplicity, let's ignore the electron's spin and focus on the coordinate-space wave functions, so there are four states at play, one 2s state and three 2p states.

- (a) Consider the  $4 \times 4$  matrix elements of  $\delta \hat{H}$  between these 4 states. Show that for the electric field pointing in the  $z$  direction, 14 out of 16 matrix elements vanish, with the only 2 non-vanishing matrix elements being

$$\langle 2s | \delta \hat{H} | 2p, m = 0 \rangle \quad \text{and} \quad \langle 2p, m = 0 | \delta \hat{H} | 2s \rangle. \quad (2)$$

- (b) Calculate these 2 matrix elements. For your convenience, eqs. (22) through (25) at the end of this homework set spell out the normalized wave-functions of the hydrogen atom's 1s, 2s, and 2p states.
- (c) Calculate the energies of the four  $n = 2$  states — or their linear combinations — to the first order in the electric field.

(d) What happens to these energies when the electric field has a different direction?

In real life, the 2s and 2p state of the hydrogen atom are not exactly degenerate, and the electron's spin interacts with the orbital angular momentum. Taking the spin into account, we have  $4 \times 2 = 8$  states at the  $n = 2$  level, and in the absence of the electric field they have 3 slightly different energy levels for different  $\ell$  and  $j$ . Specifically,

$$\begin{aligned} E(2p, j = \frac{3}{2}) - E(2p, j = \frac{1}{2}) &= \Delta E_{\text{fine structure}} \approx 45 \mu\text{eV}, \\ E(2s, j = \frac{1}{2}) - E(2p, j = \frac{1}{2}) &= \Delta E_{\text{Lamb shift}} \approx 4.37 \mu\text{eV}. \end{aligned} \quad (3)$$

Consequently, the linear Stark effect is truly linear only when it yields energy differences much bigger than the fine structure or the Lamb shift,

$$\delta E(\text{Stark}) \gg \delta E(\text{fine structure}) > \delta E(\text{Lamb shift}). \quad (4)$$

Otherwise, we need to treat the electric field, the fine structure, and the Lamb shift as comparable perturbations comprising

$$\delta \hat{H}_{\text{net}} = \delta \hat{H}_{\text{fine structure}} + \delta \hat{H}_{\text{Lamb shift}} - \vec{\mathcal{E}} \cdot \hat{\mathbf{d}}, \quad (5)$$

and then diagonalize the  $8 \times 8$  matrix of this  $\delta \hat{H}_{\text{net}}$  between the eight  $n = 2$  states.

(e) Show that this  $8 \times 8$  matrix is block diagonal with two trivial  $1 \times 1$  blocks and two non-trivial  $3 \times 3$  blocks. Spell out the  $3 \times 3$  blocks, and argue that their eigenvalues are non-linear functions of the electric field except in the strong-field regime (4). But don't try to diagonalize the  $3 \times 3$  blocks, that would take too much work.

Hint: for simplicity, assume the electric field pointing in the  $z$  direction.

Numerically, the eigenvalues become approximately linear functions of the electric field  $\mathcal{E}$  — and thus the linear Stark effect becomes truly linear — for

$$\delta E(\text{Stark}) \gtrsim \delta E(\text{fine structure}). \quad (6)$$

(f) Translate this limit — and your result from part (c) — into MKSA units for the electric field. Would such a field be easily obtainable in a lab?

2. Consider 2 atoms or molecules separated by distance  $R$  that's much large than the atom's or molecule's sizes. The leading interaction between such atoms or molecules comes from the electric dipole-dipole potential

$$\delta V = \frac{(\mathbf{d}_1 \cdot \mathbf{d}_2) - 3(\mathbf{d}_1 \cdot \mathbf{n})(\mathbf{d}_2 \cdot \mathbf{n})}{R^3} \quad (7)$$

where  $\mathbf{n}$  is the unit vector in the direction of the line between the two atoms or molecules. Now suppose neither atom/molecule has an electric dipole moment in its ground state  $|\text{gr}\rangle$ ,

$$\langle \text{gr}_1 | \hat{\mathbf{d}}_1 | \text{gr}_1 \rangle = \langle \text{gr}_2 | \hat{\mathbf{d}}_2 | \text{gr}_2 \rangle = 0. \quad (8)$$

In this case, the leading force between the two atoms/molecules (each being in its ground state) is the attractive **van der Waals** force

$$\mathbf{F}_{\text{vdW}}(R) = -\frac{A\mathbf{n}}{R^7} \quad (9)$$

for some coefficient  $R$ .

In quantum mechanics, the van der Waals force — or rather the effective potential

$$V_{\text{vdW}} = -\frac{A}{6R^6} \quad (10)$$

— arises as the second-order correction to the ground state energy of two atoms/molecules in the perturbation theory where  $\delta\hat{H}$  is the dipole-dipole potential (7). Although both atoms/molecules have zero expectation values of the electric dipole moment in their ground states — and hence  $\delta E_{\text{ground}} = 0$  in the first order of the perturbation theory, — there are non-zero off-diagonal matrix elements

$$\langle \text{exc}_1 | \hat{\mathbf{d}}_1 | \text{gr}_1 \rangle \neq 0, \quad \langle \text{exc}_2 | \hat{\mathbf{d}}_2 | \text{gr}_2 \rangle \neq 0, \quad (11)$$

for some excited states  $|\text{exc}_1\rangle$  and  $|\text{exc}_2\rangle$ , which leads to the negative energy shift  $\delta E_{\text{ground}}$  in the second order of the perturbation theory.

In the perturbation theory, the unperturbed Hamiltonian  $\hat{H}_0 = \hat{H}_1 + \hat{H}_2$  where  $\hat{H}_1$  is the Hamiltonian for the standalone first atom or molecule and likewise  $\hat{H}_2$  is the Hamiltonian of the standalone second atom/molecule, so the eigenstates of the  $\hat{H}_0$  have general form  $|\text{state}_1; \text{state}_2\rangle$ . The interactions between the two atoms/molecules comes from the perturbation by  $\delta H = \delta V_{\text{dipole-dipole}}$  as in eq. (7).

(a) Show that in the second order of the perturbation theory

$$\delta E_{\text{ground}} = -\frac{A}{6R^6} \quad (12)$$

for

$$\frac{A}{6} = \sum_{|\text{exc}_1\rangle} \sum_{|\text{exc}_2\rangle} \frac{\left| \langle \text{exc}_1 | \hat{d}_1^i | \text{gr}_1 \rangle \langle \text{exc}_2 | \hat{d}_2^j | \text{gr}_2 \rangle (\delta^{ij} - 3n^i n^j) \right|^2}{E(\text{exc}_1) + E(\text{exc}_2) - E(\text{gr}_1) - E(\text{gr}_2)}. \quad (13)$$

Note: to keep my formulae from becoming unwieldy, I use  $\sum_{|\text{exc}\rangle}$  to denote the discrete sum over the bound excited states plus the integral over the un-bound states.

Next, suppose that the ground states of both atoms/molecules have  $L = 0$ .

(b) Show that in this case, the excited states with non-zero contributions to the sum (13) must have  $L(\text{exc}_1) = L(\text{exc}_2) = 1$  as well as  $S(\text{exc}_1) = S(\text{gr}_1)$  and  $S(\text{exc}_2) = S(\text{gr}_2)$ .

For simplicity, let's ignore the fine structure of the excited energy levels, so all the excited states have definite  $m_L$  and  $M_S$ , and we may focus on the excited states with  $M_S(\text{exc}) = m_S(\text{gr})$  only. Also, without the fine structure, the energies  $E(\text{exc}_1)$  and  $E(\text{exc}_2)$  in the denominators of each term in the sum (13) do not depend on the  $m_L$  quantum numbers of the excited states, and this allows us to sum over the  $m_L(\text{exc}_1)$  and  $m_L(\text{exc}_2)$  before we sum over the rest of the excited states' quantum numbers.

(c) Use Wigner–Eckart theorem to sum over the  $m_L$  quantum numbers of the excited states in the sum (13) as well as over the indices  $i, j$  of the dipole moment components and show that

$$\frac{A}{6} = 6 \sum_{|\text{exc}_1\rangle \in \text{set}_1} \sum_{|\text{exc}_2\rangle \in \text{set}_2} \frac{\left| \langle \text{exc}_1 | \hat{d}_1^z | \text{gr}_1 \rangle \right|^2 \times \left| \langle \text{exc}_2 | \hat{d}_2^z | \text{gr}_2 \rangle \right|^2}{E(\text{exc}_1) + E(\text{exc}_2) - E(\text{gr}_1) - E(\text{gr}_2)} \quad (14)$$

where

$$\begin{aligned} \text{set}_1 &= \{\text{eigenstates of } \hat{H}_1 \text{ with } L = 1, m_L = 0, S = S(\text{gr}_1), m_S = m_S(\text{gr}_1)\}, \\ \text{set}_1 &= \{\text{eigenstates of } \hat{H}_2 \text{ with } L = 1, m_L = 0, S = S(\text{gr}_2), m_S = m_S(\text{gr}_2)\}. \end{aligned} \quad (15)$$

Hint: for atoms/molecules in the ground states with  $L = 0$ ,  $A$  does not depend on the direction  $\mathbf{n}$ , so let it point in the  $z$  direction. Then use spherical components for the electric dipole vectors  $\hat{\mathbf{d}}_1$  and  $\hat{\mathbf{d}}_2$ , so that

$$\begin{aligned} \mathbf{n} \cdot \hat{\mathbf{d}}_1 &= \hat{d}_1^z = \hat{d}_1^0, \\ \mathbf{n} \cdot \hat{\mathbf{d}}_2 &= \hat{d}_2^z = \hat{d}_2^0, \\ \hat{\mathbf{d}}_1 \cdot \hat{\mathbf{d}}_2 &= \sum_{\mu=-1}^{+1} (-1)^\mu \hat{d}_1^{+\mu} \hat{d}_2^{-\mu} = -\hat{d}_1^{-1} \hat{d}_2^{+1} + \hat{d}_1^0 \hat{d}_2^0 - \hat{d}_1^{+1} \hat{d}_2^{-1}. \end{aligned} \quad (16)$$

Now let's consider the van der Waals force between two hydrogen atoms. For simplicity, let's ignore the fine structure of the excited states, so we may use the  $|n, \ell, m_\ell, m_s\rangle$  basis for the bound states, and a similar basis for the unbound states with definite  $\ell$ ,  $m_\ell$ , and  $m_s$ . Moreover, the spin state  $m_s$  does not affect the matrix elements of the dipole moment (as long as we have the same  $m_s$  on the bra side and the ket side), so we may ignore them in our calculations. Thus, we label the excited states by  $n$ ,  $\ell$ , and  $m = m_\ell$  where by abuse of notations  $n$  runs over both discrete values  $n = 2, 3, 4, \dots$  for the bound excited states as well as some continuous values for the unbound states. In these notations,

$$\text{set}_1 = \text{set}_2 = \{|n, \ell, m\rangle \text{ with } \ell = 1, m = 0, \text{ and any } n \neq 1\}, \quad (17)$$

so the sum (14) becomes

$$\frac{A}{6} = 6 \sum_{n_1 \neq 1} \sum_{n_2 \neq 1} \frac{|\langle n_1, 1, 0 | \hat{d}^z | 1, 0, 0 \rangle|^2 \times |\langle n_2, 1, 0 | \hat{d}^z | 1, 0, 0 \rangle|^2}{E(n_1) + E(n_2) - 2E(n = 1)}. \quad (18)$$

(d) Put upper and lower bounds on the sum (18). Specifically, show that

$$A_{\min} < A < A_{\max} \quad (19)$$

for

$$\frac{A_{\min}}{6} = \frac{3}{E(n=2) - E(n=1)} \times \left| \langle 2, 1, 0 | \hat{d}^z | 1, 0, 0 \rangle \right|^4, \quad (20)$$

$$\frac{A_{\max}}{6} = \frac{3}{E(n=2) - E(n=1)} \times \left( \langle 1, 0, 0 | (\hat{d}^z)^2 | 1, 0, 0 \rangle \right)^2. \quad (21)$$

(e) Finally, evaluate the matrix elements in eqs. (20) and (21), and calculate the upper and lower bounds for the van der Waals coefficient  $A$ . For your convenience, eqs. (22) through (25) below spell out the wave-functions of the relevant states of the hydrogen atom.

★ For your convenience, here are the wave functions of the 1s, 2s, and 2p states of the hydrogen atom:

$$\Psi_{1s}(\mathbf{x}) = \frac{1}{\sqrt{\pi a^3}} \times \exp(-r/a), \quad (22)$$

$$\Psi_{2s}(\mathbf{x}) = \frac{1}{\sqrt{32\pi a^5}} \times \exp(-r/2a) \times (2a - r), \quad (23)$$

$$\Psi_{2p}^{m=0}(\mathbf{x}) = \frac{1}{\sqrt{32\pi a^5}} \times \exp(-r/2a) \times r \cos \theta, \quad (24)$$

$$\Psi_{2p}^{m=\pm 1}(\mathbf{x}) = \frac{1}{\sqrt{32\pi a^5}} \times \exp(-r/2a) \times \frac{\mp 1}{\sqrt{2}} r \sin \theta \exp(\pm i\phi), \quad (25)$$

where  $a$  is the Bohr radius

$$a = \frac{\hbar^2}{m_e e^2} \approx 0.53 \text{ \AA} = 5.3 \cdot 10^{-11} \text{ m}. \quad (26)$$